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(54) Process for continuous production of ethylene-vinyl acetate copolymer.

(57) An improved process for continuously producing ethylene-vinyl acetate copolymer containing 20 to 50 mol% of ethylene is provided. The process of this invention permits the stable production of the copolymer over a long period of time.

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PROCESS FOR CONTINUOUS PRODUCTION OF ETHYLENE-VINYL ACETATE COPOLYMER

The present invention relates to a process for producing ethylene-vinyl acetate copolymer continuously in the very stable manner over a long period of time.

Much has been studied so far on the technology that permits stable production of ethylene-vinyl acetate copolymer over a long period of time; but no satsifactory one has been found. The key to the stable continuous operation is how to remove a large amount of reaction heat generated during the copolymerization of ethylene and vinyl acetate. There are several ways of removing the reaction heat. In one way, reaction heat is removed by means of a jacket and coil provided on and in the polymerization vessel. In another way, reaction heat is removed by circulating the reaction liquid through a cooler installed outside the vessel. In still another way, reaction heat is removed by introducing ethylene gas, which is present in the upper space of the vessel, into a cooler installed outside the vessel, and returning the cooled or condensed ethylene to the vessel. These methods however, have the following drawbacks.

(1) Drawbacks involved in the way of removing reaction heat by means of jacket and coil attached to the polymerization vessel.

(a) With the lapse of operation time, polymer deposits on the surfaces of the jacket and coil, reducing their capability of heat conduction. To continue operation, the polymer deposit has to be washed out from the jacket and coil. This requires periodic shut-down.

(b) The flow of the reaction liquid is inevitably poor in the space between the pipes of the coil and the space between the coil and the vessel wall. This leads to the formation of gel and lump that adversely affects the quality of the resulting polymer.

(2) Drawbacks involved in the way of removing reaction heat by means of the circulating cooler for the reaction liquid.

(a) As with the above case, polymer deposits on the heat transfer area of the circulating cooler with the lapse of operation time, reducing the capability of heat conduction. To continue operation, it is necessary to remove the polymer deposit or to install the cooler in duplicate for alternate use. The former requires periodic shut-down.

(b) Since the reaction solution is highly viscous, the circulation of it causes a great deal of pressure loss. Cooling by the evolution of sensible heat requires the circulation of a large amount of reaction solution. This leads to the consumption of a large amount of pumping energy. Pumping under high pressure often causes leakage from the seal. The leaked solution releases ethylene gas and solidifies on the equipment, entailing a danger and creating a difficulty in equipment maintenance.

(c) The high viscosity of the reaction solution makes it difficult to increase the flow rate, and the low thermal conductivity of the reaction solution requires the cooler to have a large heat transfer area.

(d) No coolers achieve the complete piston flow because of the structure, and the hold-up in the dead space is inevitable where gel and lump detrimental to the quality are formed.

(3) Drawbacks involved in removing reaction heat by cooling and condensing ethylene gas.

(a) The condensing temperature of ethylene is low (particularly when the pressure is low) and the condensing of ethylene is only possible by the aid of a cooling medium at an extremely low temperature.

(b) Since ethylene gas to be cooled has only a small amount of sensible heat, it is necessary to circulate a large amount of ethylene gas by using a booster.

(c) The condensing of ethylene is impossible to perform under a pressure higher than that (50.5 atm) at the critical point.

(d) As the state of ethylene approaches the critical point, the difference in enthalpy and density becomes small between gaseous ethylene and liquefied ethylene. This makes difficult the condensing operation.

It is an object of this invention to provide a process for continuous production of ethylene-vinyl acetate copolymer which is free of the above-mentioned drawbacks.

The subject matter of this invention is an improved process for continuously producing ethylene-vinyl acetate copolymer containining 20 to 50 mol% of ethylene by introducing ethylene, vinyl acetate, solvent, and polymerization catalyst into a polymerization vessel, which is characterized in that

(1) vinyl acetate or a solvent solution of vinyl acetate is passed through a heat exchanger provided with a cooling means, and simultaneously ethylene discharged from the polymerization vessel is passed through said heat exchanger,

so that they come into contact with each other in said heat exchanger, whereby causing the vinyl acetate or the solvent solution of vinyl acetate to absorb and solubilize ethylene,

(2) the vinyl acetate or the solvent solution of vinyl acetate which has absorbed and solubilized ethylene therein is introduced into the polymerization vessel, and

(3) the vinyl acetate or the solvent solution of vinyl acetate which has absorbed and solubilized ethylene therein is mixed in the polymerization vessel with the polymerization solution, the polymerization solution is heated up to the prescribed polymerization temperature, at which ethylene is vaporized from the vinyl acetate or the solvent solution of vinyl acetate by the aid of the heat in the polymerization vessel, and the vaporized ethylene is circulated to the heat exchanger.

(a) Since the heat transfer surface of the heat exchanger does not come into contact with the polymer, it does not suffer from a decrease of heat conduction capability due to polymer deposit. This permits the stable production of ethylene-vinyl acetate copolymer over a long period of time.

(b) It is not necessary to install a cooling coil in the polymerization vessel, or a small one is sufficient, if any. This eliminates or minimizes the dead space in which gel and lump are liable to occur.

(c) The heat exchanger can be of any size as required. Thus it is possible to employ a polymerization vessel of large size.

(d) The difference in the densities of liquid and gas can be utilized for circulation. This obviates the installation of pumps and boosters, making the facilities simpler.

(e) The process involves both condensation and solution; in other words, the process utilizes both heat of condensation and heat of solution. Thus there is a great difference between the enthalpy of gaseous ethylene and the enthalpy of liquid ethylene. This makes it possible to reduce the quantity of ethylene for circulation.

(f) The critical point (both pressure and temperature) of ethylene in the two-component system of ethylene and vinyl acetate is higher than that in the system of ethylene alone. This provides a broad operating range for condensing ethylene and permits the use of a coolant at a high temperature. In addition, there is a great difference between the enthalpy of gaseous ethylene and the enthalpy of liquid ethylene. This makes it possible to reduce the quantity of ethylene for circulation.

Fig. 1 is a schematic drawing illustrating the process of this invention and an example of the apparatus used in this invention. Each reference numeral denotes the following.

1 ... Polymerization vessel
2 ... Polymerization solution
3 ... Space 4 ... Stirrer
5 ... Inlet for ethylene gas
6 ... Inlet for polymerization catalyst
7 ... Connecting line 8 ... Connecting line
9 ... Vertical wetted-wall multi-tubular heat exchanger
10 ... Tube 11 ... Outside of tube
12 ... Inlet for vinyl acetate
13 ... Outlet for inert gas
14 ....Outlet for coolant
15 ... Inlet for coolant 16 ... Valve
17 ... Outlet for polymerization reaction mixture

The preferred heat exchanger to be used in this invention is a vertical wetted-wall heat exchanger, particularly a vertical wetted-wall multi-tubular heat exchanger. It also includes those which have a large surface area, such a structure that permits absorption of ethylene gas, and an ability to transfer heat rapidly. Examples of such heat exchangers include one which is made up of an absorber of packed column type, perforated plate type, or bubble cap tower type, and a jacket, and/or a coil.

As mentioned above, vinyl acetate or a solvent solution of vinyl acetate (referred to as simply vinyl acetate hereinafter) and ethylene are passed through the heat exchanger equipped with a cooling means, in which vinyl acetate and ethylene come into contact with each other and ethylene is absorbed by and solubilized in vinyl acetate, and the heat of condensation and the heat of solution are removed. To put it concretely, vinyl acetate is allowed to flow in the form of thin film along the inside of the tube of the vertical wetted-wall multi-tubular heat exchanger, and simultaneously ethylene gas is passed through the tube so that ethylene is absorbed by and solubilized in vinyl acetate. The heat of condensation and the heat of solution are removed by the coolant flowing outside the tube.

Vinyl acetate should be fed to the heat exchanger as much as necessary for the amount of heat to be removed. Thus it is possible to feed a part of vinyl acetate directly to the polymerization vessel. Also, a part of solvent may be used for dissolving the polymerization catalyst, and vinyl acetate may be fed into the polymerization vessel together with the polymerization catalyst.

The vinyl acetate which has absorbed ethyene (referred to as absorption liquid hereinafter) should be cooled to a temperature T_1 in the range of $-20°C \leq T_1 < T_2$, preferably $-10°C \leq T_1 \leq T_2 - 10°C$, wherein T_2 is the polymerization temperature, before being introduced into the polymerization vessel. If T_1 is higher than T_2, it is industrially nonsense because heat removal is not achieved in the polymerization vessel. The process of this invention is effective only when a proper temperature is chosen so that ethylene gas condenses. Thus T_1 should be above the temperature at which gaseous ethylene and liquid ethylene can coexist under a certain polymerization pressure. In other words, T_1 should be above the temperature at which the saturated vapor pressure of ethylene coincides with the polymerization pressure of ethylene. For example, T_1 should be above -28°C if the polymerization pressure is about 21 bar (20 kg/cm^2G), and above 0°C at about 41 bar (40 kg/cm^2G). In consideration of the fluctuations that will occur in the actual operation, the temperature should be set up with some tolerance. Thus in the process of this invention, T_1 should be above -20°C, and preferably above -10°C for the polymerization pressure in the range of about 21 to 71 bar (20 to 70 kg/cm^2G). In the meantime, it is known that the critical pressure of ethylene is about 50.5 bar, and it is higher than this when ethylene coexists with vinyl acetate. And it has been confirmed that there is a region in which both gas and liquid coexist under the polymerization pressure of about 71 bar (70 kg/cm^2G) employed in this invention. The T_1 for the absorption liquid is determined according to the amount of heat to be removed and the polymerization pressure. As the polymerization pressure increases, the lower limit of T_1 becomes high, and consequently the amount of heat that can be removed decreases accordingly.

The solvent used in this invention includes lower aliphatic alcohols of carbon number 1 to 4; and industrially preferable among them is methanol. Where a copolymer of high degree of polymerization is to be obtained, tertiary butanol or a mixture of tertiary butanol and methanol is preferable.

The absorption liquid is introduced into the polymerization vessel in which it is mixed with the polymerization solution. While the absorption liquid is heated up to the prescribed polymerization temperature by reaction heat, ethylene in excess of solubility is vaporized from the absorption liquid, and the vaporized ethylene is returned to the heat exchanger in which it is absorbed by and solubilized in vinyl acetate. Thus the cycle of the absorption and solubilization of ethylene in the heat exchanger and the vaporization of ethylene in the polymerization vessel is completed for the removal of reaction heat from the polymerization system. This is what produces the above-mentioned beneficial effects of this invention.

The polymerization temperature T_2 should preferably be lower than 80°C, because as it goes up, the resulting ethylene-vinyl acetate is low in the degree of polymerization. Although the polymerization temperature should preferably be low from the standpoint of the degree of polymerization, it should be higher than 35°C because the rate of polymerization decreases as the polymerization temperature goes down. The preferred polymerization temperature is 40 to 70°C.

The polymerization temperature and the amount of heat to be removed can be properly adjusted by controlling the temperature of the polymerization solution, the temperature of absorption liquid to be introduced into the polymerization vessel, and the temperature and volume of the coolant.

The solvent in the polymerization vessel should be used in as small a quantity as possible if it is desirable to obtain ethylene-vinyl acetate copolymer having a comparatively high degree of polymerization which is suitable for molding. The quantity of solvent should preferably be 1 to 30 wt% (based on the total liquid), and more preferably 1 to 20 wt%.

The polymerization in the process of this invention may be accomplished by the use of a single vessel or two or more vessels connected in series.

The polymerization pressure is determined according to how much ethylene should be contained in the resulting ethylene-vinyl acetate copolymer. In this invention, it is about 21 to 71 bar (20 to 70 kg/cm^{2}G) since the invention is designed to give ethylene-vinyl acetate copolymers containing 20 to 50 mol% of ethylene. In the polymerization of the desired ethylene-vinyl acetate copolymer, it is essential that dissolved ethylene is present in the solvent solution of vinyl acetate in the polymerization vessel. The ethylene concentration should be higher as the desired ethylene content in ethylene-vinyl acetate copolymer is higher. This means that high pressure is required for the production of copolymers of high ethylene content, and low pressure for copolymers of low ethylene content.

Almost any kind of radical polymerization initiator can be used as the polymerization catalyst in the process of this invention. Preferred examples include azo compounds such as 2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis-(2,4-dimethylvaleronitrile), and 2,2'-azobis-isobutylonitrile; alkyl peresters such as t-butyl perpivalate; peroxy dicarbonates such as bis-(4-t-butyl-cyclohexyl)peroxy-di-carbonate and dicyclohexyl peroxy-di-carbonate; and peroxides such as dilauloyl peroxide. The polymerization catalyst may be charged in the form of solution in a part of the solvent to be charged into the vessel.

Although the invention is intended to produce mainly ethylene-vinyl acetate copolymers, it permits the production of copolymers containing a third component. The third component is a copolymerizable comonomer, preferred examples of which include olefins such as propylene and isobutylene; unsaturated acids or esters thereof such as crotonic acid, acrylic acid, methacrylic acid, and maleic acid; and vinyl esters other than vinyl acetate such as vinyl propionate and vinyl ester of versatic acid. The content of the third component in the copolymer is less than 10 mol%. The third component may be introduced into the vessel together with ethylene or the solvent solution of vinyl acetate, if soluble therein.

The invention is now described with reference to the accompanying single drawing illustrating the process of this invention and an example of the apparatus employed in this invention.

Ethylene gas under a prescribed pressure is introduced into the vessel (1) through the line (5). Simultaneously, a polymerization catalyst or a solution of polymerization catalyst (referred to as catalyst solution hereinafter) is introduced into the vessel (1) through the line (6). Ethylene gas may be introduced into the vessel (1) through other parts than the line (5), that is, through the lower part of the below-mentioned heat exchanger (9), or through the connecting line (7) or (8) installed between the vessel (1) and the heat exchanger (9). Further catalyst solution may be introduced into the vessel (1) through other connecting line (8) than the inlet line (6).

On the other hand, vinyl acetate is introduced into the vertical wetted-wall multi-tubular heat exchanger (9) through the line (12). The vinyl acetate is allowed to flow in the form of thin film along the inside of the tube (10). Ethylene gas present in the space (3) of the vessel (1) is introduced into the heat exchanger (9) through the line (7). The ethylene gas rises through the tube (10) countercurrently to and in contact with vinyl acetate. Thus the ethylene gas is absorbed in and solubilized in vinyl acetate, preferably to saturation. If necessary, a part of vinyl acetate may be introduced directly into the vessel (1).

The coolant is introduced into the heat exchanger (9) through the line (15). The coolant is allowed to flow through the space (11) outside the tube (10), so that it removes the heat of condensation and solution of ethylene which is generated as ethylene is absorbed by and solubilized in vinyl acetate. The coolant is discharged from the outlet (14). Inert gases are discharged from the top of the heat exchanger (9) through the line (13).

The vinyl acetate which has absorbed ethylene and has been cooled in the heat exchanger (9) is introduced into the vessel (1) through the line (8). (The line (7) and the line (8) may be combined to form a single line.) The vinyl acetate (absorption liquid) introduced into the vessel is mixed with the polymerization solution (2) and heated to the prescribed polymerization temperature. During the heating, the absorption liquid vaporizes ethylene dissolved in excess of the solubility in vinyl acetate. The vaporized ethylene is circulated again to the heat exchanger through the line (7).

The polymerization temperature is adjusted by controlling the temperature of the absorption liquid to be introduced from the heat exchanger (9) into the polymerization vessel (1) through the line (8). The temperature of the absorption liquid is adjusted by controlling the valve (16) for the coolant to be introduced into the heat exchanger (9).

The polymerization vessel (1) is installed with the stirrer (4). The solution polymerization is carried out for a prescribed period of time, and the resulting polymerization reaction mixture is discharged through the line (17). Ethylene-vinyl acetate copolymer is separated from the polymerization reaction mixture. The copolymer thus obtained may be saponified in the usual way with a caustic alkali (e.g. caustic soda) or an alkali metal alcoholate (e.g. sodium methylate) catalyst in a solvent, and the saponified product may be molded into various forms.

As mentioned above, the process of this invention makes it possible to produce ethylene-vinyl acetate copolymer continuously over a long period of time without the deposit of polymer and the formation of gel in the polymerization vessel. As demonstrated in the following examples, continuous operation over 90 days is possible when the process of this invention is employed, whereas the conventional process requires shut-down for cleaning every ten days. Thus the present invention is of great industrial significance.

The invention is now described in more detail with reference to the non-limitative examples and comparative examples that follow.

EXAMPLES 1 to 3

Ethylene-vinyl acetate copolymer was produced continuously by using an apparatus as shown in Fig. 1. The polymerization vessel has a volume of 660 liters, and the heat exchanger has a heat transfer area of 3 m^2 and 8 tubes. The polymerization vessel has no coil therein, so that the removal of heat is accomplished by the heat exchanger. The solvent was methanol and the coolant was a 30 wt% aqueous solution of methanol. The polymerization conditions and the results are shown in Table 1.

Items	Unit	Example 1	Example 2	Example 3
Polymerization pressure	bar	41	39	58
Polymerization temperature T_2	°C	55	50	55
Feed of ethylene	kg/hr	5.2	8.2	14
Feed of vinyl acetate	kg/hr	27	43	34
Composition: Vinyl acetate	wt%	100	88	100
Methanol	wt%	0	12	0
Feed of absorption liquid	kg/hr	107	117	130
Composition: Vinyl acetate	wt%	25	32	26
Methanol	wt%	0	5	0
Ethylene	wt%	75	63	74
Methanol directly fed to vessel	kg/hr	2.0	1.3	4.5
Polymerization catalyst		Note 1	Note 1	Note 2
Temperature T_1 of absorption liquid	°C	3.0	7.0	28
Polymerization reaction mixture				
Discharge rate	kg/hr	34	53	53
Composition: Copolymer	wt%	45	25	20
Vinyl acetate	wt%	40	50	50
Ethylene	wt%	9	12	22
Methanol	wt%	6	13	8
Circulation of coolant	m^3/hr	1.5	1.8	1.6
Temperature of incoming coolant	°C	-3.0	-2.5	-3.0
Amount of heat removed by heat exchanger	MJ/hr	24.1	22.3	22.0
Number of days of continuous operation	days	90	92	100
Content of ethylene in copolymer	mol%	30	29	40

Note 1: 2,2'-azobisisobutyronitrile

Note 2: t-butyl perpivalate

It is to be noted from Table 1 that in the examples continuous operation for more than 90 days was carried out according to the process of this invention. The inspection after shut-down revealed that there was almost no polymer deposit on the walls of the vessel and the shaft of the stirrer. Almost no gel was found in the resulting ethylene-vinyl acetate copolymer.

COMPARATIVE EXAMPLES 1 to 3

Continuous polymerization was carried out under the same conditions as in Examples 1 to 3, except that the vertical wetted-wall multi-tubular heat exchanger was not used but the polymerization vessel was provided with a jacket and coil. The volume of the vessel was 600 liters, and the heat transfer area of the jacket and coil was 3 m^2. The removal of heat was accomplished by circulating a fixed amount of water through the jacket and coil and replenishing water at a proper flow rate in accordance with the amount of heat to be removed. Excess water was discharged by overflowing. The results are shown in Table 2.

Table 2

Items	Unit	Comparative Example 1	Comparative Example 2	Comparative Example 3
Polymerization pressure	bar	41	39	58
Polymerization temperature T_2	°C	55	50	55
Feed of ethylene	kg/hr	5.2	8.2	14
Feed of vinyl acetate	kg/hr	27	38	34
Feed of methanol	kg/hr	2	7	5
Polymerization catalyst		Note 1	Note 1	Note 2
Polymerization reaction mixture				
Discharge rate	kg/hr	34	53	53
Composition: Copolymer	wt%	45	25	20
Vinyl acetate	wt%	40	50	50
Ethylene	wt%	9	12	22
Methanol	wt%	6	13	8
Temperature of replenishing coolant	°C	28	22	25
Average temperature of fed and discharged coolant **	°C	45→35	42→25	45→35
Number of days of continuous operation	days	10	11	11
Amount of heat removed by heat exchanger	MJ/hr	24.0	22.2	21.9

Note 1: 2,2'-azobisisobutyronitrile

Note 2: t-butyl perpivalate

** This indicates that the temperature of the coolant was lowered as the duration of operation was extended.

It is to be noted from Table 2 that after continuous operation for about ten days the difference between polymerization tempeature T_2 and average temperature of fed and discharged coolant became gradually greater and it became 20 to 25°C, and at last average temperature of fed and discharged coolant came close to that of the replenishing coolant.

This means that it was impossible to continue operation any longer. The inspection after shut-down revealed that there was a large amount of lump of polymer deposited on the surface of the jacket and coil and the shaft of the stirrer. Gel was found in the resulting ethylene-vinyl acetate copolymer.

Claims

1. A process for continously producing ethylene-vinyl acetate copolymer containining 20 to 50 mol% of ethylene by introducing ethylene, vinyl acetate, solvent, and polymerization catalyst into a polymerization vessel, characterized in that

(1) vinyl acetate or a solvent solution of vinyl acetate is passed through a heat exchanger provided with a cooling means, and simultaneously ethylene discharged from the polymerization vessel is passed through said heat exchanger, so that they come into contact with each other in said heat exchanger, whereby causing the vinyl acetate or the solvent solution of vinyl acetate to absorb and solubilize ethylene,

(2) the vinyl acetate or the solvent solution of vinyl acetate which has absorbed and solubilized ethylene therein is introduced into the polymerization vessel, and

(3) the vinyl acetate or the solvent solution of vinyl acetate which has absorbed and solubilized ethylene therein is mixed in the polymerization vessel with the polymerization solution, the polymerization solution is heated up to the prescribed polymerization temperature, at which ethylene is vaporized from the vinyl acetate or the solvent solution of vinyl acetate by the aid of the heat in the polymerization vessel, and the vaporized

ethylene is circulated to the heat exchanger.

2. The process according to claim 1, characterized in that vinyl acetate or a solvent solution of vinyl acetate is allowed to flow down in the form of thin film in the heat exchanger provided with a cooling means.

3. The process according to claim 1, characterized in that vinyl acetate or a solvent solution of vinyl acetate is allowed to flow down in the form of thin film along the internal surface of the tube of a wetted-wall multi-tubular heat exchanger and a coolant is allowed to pass outside the tube.

4. The process according to claim 1, characterized in that the following inequality is established:

$$-20 \leqq T_1 < T_2$$

where T_1 is the temperature (°C) of vinyl acetate or a solvent solution of vinyl acetate being introduced into the polymerization vessel which has absorbed and solubilized ethylene therein; and T_2 is the polymerization temperature (°C) in the polymerization vessel.

Fig. 1